ORGANIC CARBON, INORGANIC CARBON, AND RELATED VARIABLES IN OFFSHORE OIL PRODUCTION AREAS OF THE NORTHERN GULF OF MEXICO

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ABSTRACT

Analyses of over 700 surface and water column samples taken from Timbalier Bay and the offshore area from the South Timbalier Field eastward toward Grand Isle, Louisiana, revealed an ecosystem rich in organic carbon (OC). Total organic carbon (TOC) averaging 5 mg/l is experienced on the near continental shelf of this region, in sharp contrast with the waters of the open Gulf, which average 1.5 to 2 mg/l.

Another large increase in TOC is experienced as one moves inshore into Timbalier Bay where mean values exceed 9 mg/l, occasionally ranging from 15 to 20 mg/l. During certain seasons or on certain sampling trips, the presence of a production platform or workover rig can be noted by increased OC values or biochemical oxygen demand (BOD), particularly in Timbalier Bay where surface sampling is possible.

Several local factors peculiar to this area of the Gulf contribute to (1) a heavy organic load, (2) effects on dissolved oxygen (DO), and (3) occasional ecological instabilities on the continental shelf off Grand Isle. The Mississippi River Plume, the extensive tidal marshes of South Louisiana, the large shallow water bays, the oil industry, and a clockwise eddy current off Grand Isle all contribute to conditions under which oxygen depletion can occur on the continental shelf. In the summer of 1973, following heavy spring flooding, "fresh" water from the

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Mississippi plume overlay the Gulf waters below it to a depth of 7 m, isolating it and allowing the oxygen content below 7 m to sag to less than 2 mg/l over most of the study area. This value is below the mean minimum DO in the deep Gulf, indicating that it is a local phenomenon, not caused by up-welling from the deep Gulf.

Vigilance should be maintained to minimize effects from oil platform effluents and operational spills because of the inherent instability of this ecosystem during spring and summer months. Plans for diverting even more water from the Mississippi River through Southwest Pass and into this area should be considered carefully before implementation.

INTRODUCTION

The dissolved organic carbon (DOC) and particulate organic carbon (POC) levels in the Atlantic Ocean and the Gulf of Mexico are difficult to reconcile on the basis of known input mechanisms of the carbon cycle. Estimates by Fredericks and Sackett (1970), based on their own results of 1961 and the data of Menzel and Ryther (1964, 1968) and of Menzel (1967), indicate DOC levels in the upper 90 m of water some 16 times the annual productivity of the Gulf of Mexico reported by El Sayed et al. (1972).

The highest values of DOC plus POC reported by Fredericks and Sackett were near 4 mg/l. The observed gradients in DOC in the upper 90 m of the Gulf could best be explained if OC inputs from rivers and estuaries were in the neighborhood of 10 to 15 mg/l. This level of OC exceeds that reported in rivers and estuaries up to the beginning of this study in 1972. Our study revealed that TOC levels emanating from terrestrial sources, estuaries, rivers, and the continental shelf, when combined with all other OC sources, are of the right order of magnitude to explain DOC gradients observed near the mouth of the Mississippi River and along the Louisiana shores.

The offshore and inshore operations areas off the Louisiana coast were chosen as areas for intensive ecological study by an interdisciplinary team of scientists belonging to member institutions of the Gulf Universities Research Consortium (GURC) early in 1972. The purpose of the Offshore Ecology Investigation (OEI) was to determine the effects, if any, of platform oil operations on the ecology of Timbalier Bay and the continental shelf immediately to the south in what is commonly referred to as the South Timbalier Field. The primary thrust of our particular project was to determine OC and related variables in surface samples in both Timbalier Bay and the offshore oil production fields. A large number of water column samples and some bottom samples were analyzed as well, for the sake of completeness. The TOC measurement was chosen because of the expected high productivity of the area and the fact that we could not predict whether oily materials would show up in the DOC or the POC.

METHODS AND PROCEDURES

Water column samples from the offshore area were taken in 2 liter Van Dorn or 5 liter Niskin water samplers. Two types of surface samplers designed and constructed at the Institute of Environmental Science, University of Southern Mississippi, worked with little or no success in the offshore area. The second sampler worked with nominal success in Timbalier Bay; however, most surface samples in Timbalier Bay were taken by lowering a bottle or cubitainer so that its neck was 0.5 cm below the surface and allowing it to fill.

Samples were quick frozen in 1-liter polyethylene bottles, 1-quart cubitainers, or polypropylene culture tubes with a capacity of 17 ml. These samples were transported still frozen to the Institute's Laboratory, where they were stored frozen, then processed within 1 or 2 days.

Processing included quick thawing (under warm water with stirring), adjusting the temperature to 25° C, blending for 30 seconds in a Waring blender, saturating with DO, and splitting the samples for BOD, OC, inorganic carbon (IC), and chemical oxygen demand (COD) determinations. One BOD bottle was used for an initial DO determination in the BOD test, and one was seeded and incubated at 20° C for 5 days for the final BOD determination. One 30 to 50 cc sample was acidified and frozen for a later COD determination, and one small sample in a 17 ml culture tube was frozen for OC and IC determinations. These tubes were used only after careful studies showed that they had no effect on TOC values of a variety of water samples, including distilled deionized CO_2-free water.

The OC and IC determinations were made on a Beckman Model 915 TOC analyzer. Twenty μl samples of OC and IC standards containing 100 mg/l carbon were injected successively into the high temperature (950° C) channel and the low temperature (150° C, acidified with H_3PO_4) channel of the TOC analyzer until the adjusted instrument provided consistent readings of 100 ± 1 ppm. Duplicate or triplicate injections of 20 μl seawater samples were then made on each channel of the TOC analyzer. After each five sample determinations, standards were injected again to check for drift or deterioration of column packings. A series of

100, 50, 30, 20, and 5 mg/l standards was injected during each continuous period of measurements to determine calibration curves or correction factors where they were significant.

The standard deviation of duplicate or triplicate total carbon determinations was $\pm$ 0.6 mg/l, with IC values agreeing to within $\pm$ 0.3 mg/l. Since OC is obtained by the difference of these results, the standard deviation is $\pm$ 0.7 mg/l carbon.

BOD determinations were made using procedures in *Standard Methods* (Menzies 1973), except that a YSI Model 54 dissolved oxygen meter was used to follow the oxygen sag during BOD tests on the last two sets of samples.

COD was determined (with little success as expected) according to procedures in *Standard Methods* on selected samples for which a high OC or BOD value was measured. Although blanks for artificial seawater were low, 25 to 30 mg/l, no consistent COD values were obtained on seawater samples.

RESULTS

Some 719 water samples taken by personnel involved in the OEI study were analyzed for organic and inorganic carbon content. Inshore samples were taken from Timbalier Bay at standard stations located around a stationary platform near Philo Brice Island, around a roving workover rig, and within a "control" area in the bay. Offshore samples were concentrated around two or three platforms in the South Timbalier field, a control area located 6 miles from the nearest rig, and two synoptic transects located between the South Timbalier platforms and Grand Isle (figure 1). Results of these analyses, which are voluminous, are stored in the GURC computerized data bank.

DISCUSSION

General observations on the whole body of data reveal that the offshore and inshore areas are two distinct but interacting systems. OC values in Timbalier Bay are nearly twice as high as values measured in the offshore region (table 1). Seasonal fluctuations in OC values and local variations around production and drilling platforms in Timbalier Bay tend to obscure the differences between control areas and areas of intensive oil operations.

Mean values of OC in Timbalier Bay are significantly higher than those measured by Brent et al. (1973) in the Bay of St. Louis, a coastal bay in Mississippi considered to be a "clean" ecosystem. That Timbalier

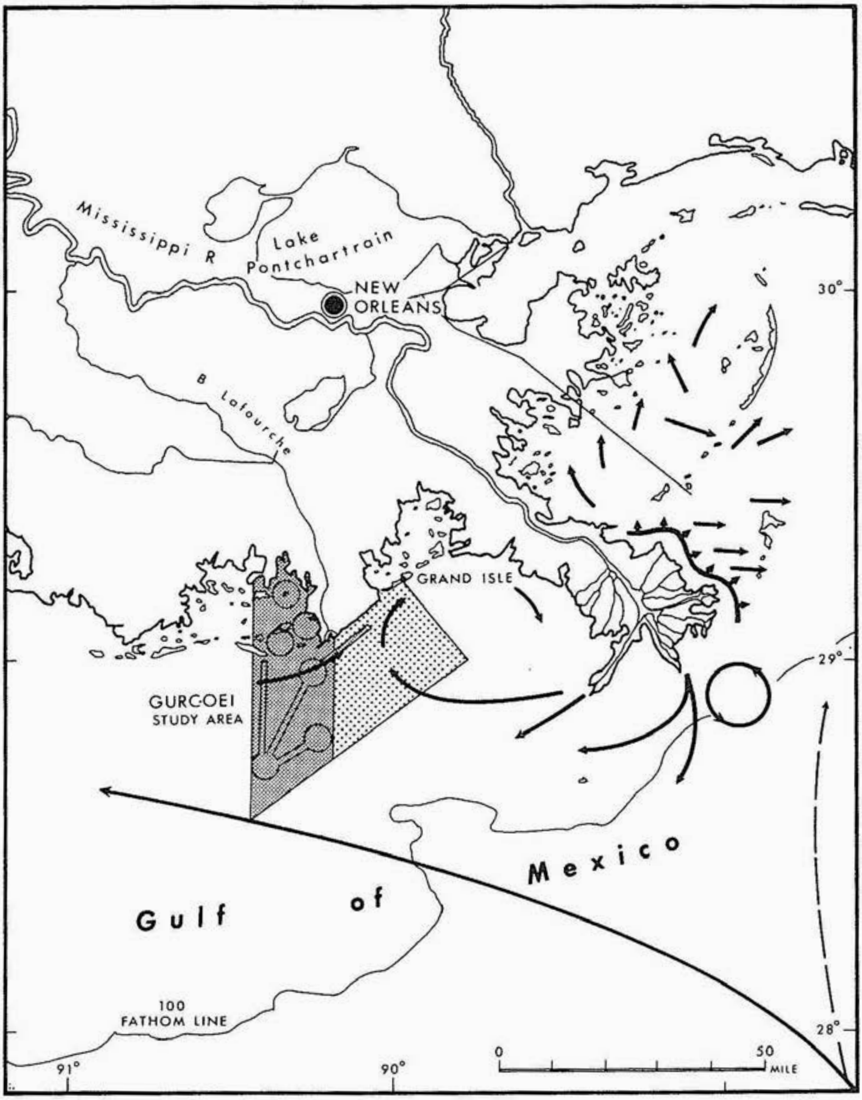

FIG. 1. GURC OEI STUDY AREA, TIMBALIER BAY, LOUISIANA. (after Harris [1974])

Bay is richer in OC can be attributed to two major factors: the extensive marshes, which feed detritus into the bay, and the presence of a major oil industry operating in the bay. That both are significant contributors to the high OC and biological productivity of the bay is shown by ancillary studies in this consortium investigation by Marum (1974), Farrell

TABLE 1. Organic Carbon and Related Variables in Selected Areas of the GURC/OEI Study

Location	Organic Carbon (mg/l)		Inorganic Carbon (mg/l)		BOD (mg/l)		COD (mg/l)	
	Mean	σ	Mean	σ	Mean	σ	Mean	σ
Timbalier Bay								
Stations Surrounding Philo Brice Platform A089 Lat 29° 11' 30" Long 90° 21' 40"	13.1	4.0	27.5	7.4	2.6	1.4	82	31
Control Area E003 Lat 29° 09' 42" Long 90° 17' 32"	9.3	1.6	27.8	3.3	1.8	0.8	102	26
Roving Work Over E042-43 Rigs South Timbalier Bay	7.8	4.2	22.6	5.7	2.0	1.0	93	29
Offshore								
Platform 54A Lat 28° 49' 57.7" Long 90° 23' 24.6"	4.5	2.0	25.2	7.6	1.1	0.8	105	39
Platform 66D Lat 28° 49' 32.8" Long 90° 22' 24.7"	5.2	3.0	22.0	5.9	1.3	1.0	68	17
Platform 26S Lat 28° 58' 46" Long 90° 10' 33"	6.1	1.5	23.2	4.7	1.4	1.1	160	45
Control Area H 062 Lat 38° 53' 30" Long 90° 18' 30"	4.9	2.2	24.6	4.4	1.2	1.1	120	34

(1974), Humm (1974), Fish and Lewis (1974), and Kritzler (1974). Although Laseter and Ledet's (1974) gas chromatography/mass spectroscopy data provided a measure of hydrocarbons present, indicating that the hydrocarbons represent only a small fraction of the measured OC, it is difficult to assess the contribution of the oil industry because of the abundance of oil-degrading bacteria populating the waters of the study sites (Oppenheimer 1974). The petroleum hydrocarbon input is certain to lose its identity as it enters the food chain. The "control" area within Timbalier Bay appears not to be isolated enough from oil industry operations to avoid all of the wind- and wave-borne effects. Clearer estimates of effects come from contours of data taken around platforms on a specific day, as will be discussed later.

Mean organic values in the offshore area of the OEI are higher by nearly 60% than those reported by Fredericks and Sackett. Since they sampled at the mouth of the Mississippi River, during only one season, the oil industry contribution to the increased OC load cannot be ascertained from comparison of their data with ours with any reasonable degree of confidence. An occurrence on the near continental shelf during the spring and summer of 1973 dramatically illustrated the importance of the interaction of OC load and spring flooding on the Mississippi. During April 1973 a synoptic study in the offshore area revealed a heavy overlay of "fresh" water in the study area (Oetking et al. 1974), with high nutrient concentrations (Burchfield et al. 1974) and evidence of an algal "bloom" in the upper layer (El-Sayed 1974). In July 1973, the "fresh" (23 g/l) water still overlay the study area to a depth of 5 to 7 m, isolating the high salinity (34 to 35 g/l) Gulf waters below that depth. Apparently, wave action was not sufficient to cause mixing below 7 m during this period. The isolation of the deep waters (7 to 20 m) and the high oxygen demand from OC loading in this area combined to produce a very low DO content, ranging from 2 mg/l immediately below the halocline to 0.5 mg/l near the bottom. Long residence times of water in this area due to a clockwise current, which was observed by Harris (1974), prevented the replenishing of DO from open Gulf waters (see figure 1). Upwelling from the deep Gulf can be excluded as a source of oxygen-depleted water because DO in the open Gulf does not fall much below 2.5 mg/l at any depth between 0 and 2500 m (El Sayed et al. 1972). Evidence of oxygen near-depletion (0.1 mg/l) also occurred in the summer of 1972, near the base of a study platform. The geological coincidence of the most highly productive offshore oil industry in the world existing in an eddy current downstream from the plume of one of the world's largest rivers leads to an ecosystem strained to the breaking point to maintain a viable DO content near the bottom during summer months following heavy flooding of the Mississippi River.

Even though the 1973 discharge from the Mississippi River was unusually high, the adjacent near continental shelf is ripe for summer seasonal fish kills, such as the one reported at the entrance of Timbalier Bay during the summer of 1973 by sampling personnel of this study. Efforts should be made to minimize OC loading and oxygen-depleted discharges near the continental shelf from Southwest Pass beyond the Timbalier Bay region, especially after heavy spring flooding. Alternatives to plans for diverting more of the outflow of the Mississippi River through Southwest Pass should be carefully considered by the best ecological expertise available before implementation of a project that might further strain this ecosystem's ability to assimilate an increased OC load. Runoff predictions would indicate that an occurrence similar to that observed in July 1973 may also have occurred in the summer of 1974.

To answer the question "does the offshore and inshore (Timbalier Bay) oil industry affect the ecosystems in which it operates?" one has to look carefully at individual sets of data taken on a given day or within the same week and at the spatial distribution of results around production and drilling platform structures. The comparison of near-platform data with control data fails to answer this question because of seasonal fluctuations and because the "control" areas are in basically the same ecosystem as the platforms. The control areas are probably exposed to spills and leakage from platforms, storage, and piping facilities through wind-driven wave transport, along with tidal and prevailing current transport.

Surface sampling, which was the only type of water column sampling done in Timbalier Bay for this study, is subject to a high degree of variability affected mostly by wave action and sampling technique. MacIntyre (1974) points out the high variability of surface samples taken by different sampling techniques as well as the wide variations in reports on the nature of the organic matter in the upper millimeter of ocean surface.

Our results show that sampling of the upper 0.5 cm of the surface can be done with reasonable consistency during calm days on Timbalier Bay. The data give smooth contours pinpointing the sources of organic pollution (figures 2, 3, 4, and 5).

The effect of the Philo Brice Platform and tank battery, Lat. 29° 11.50′, Long. 90° 21.68′, was noted on all days for which extensive OC data were taken around that site. Figure 2 shows the contours of OC data taken in September 1972 around that platform. Contours are drawn by interpolating values between measured points at 0.5 or 1.0 mg/l intervals and connecting points having the same value with smooth continuous curves. General contour shapes were checked by computer

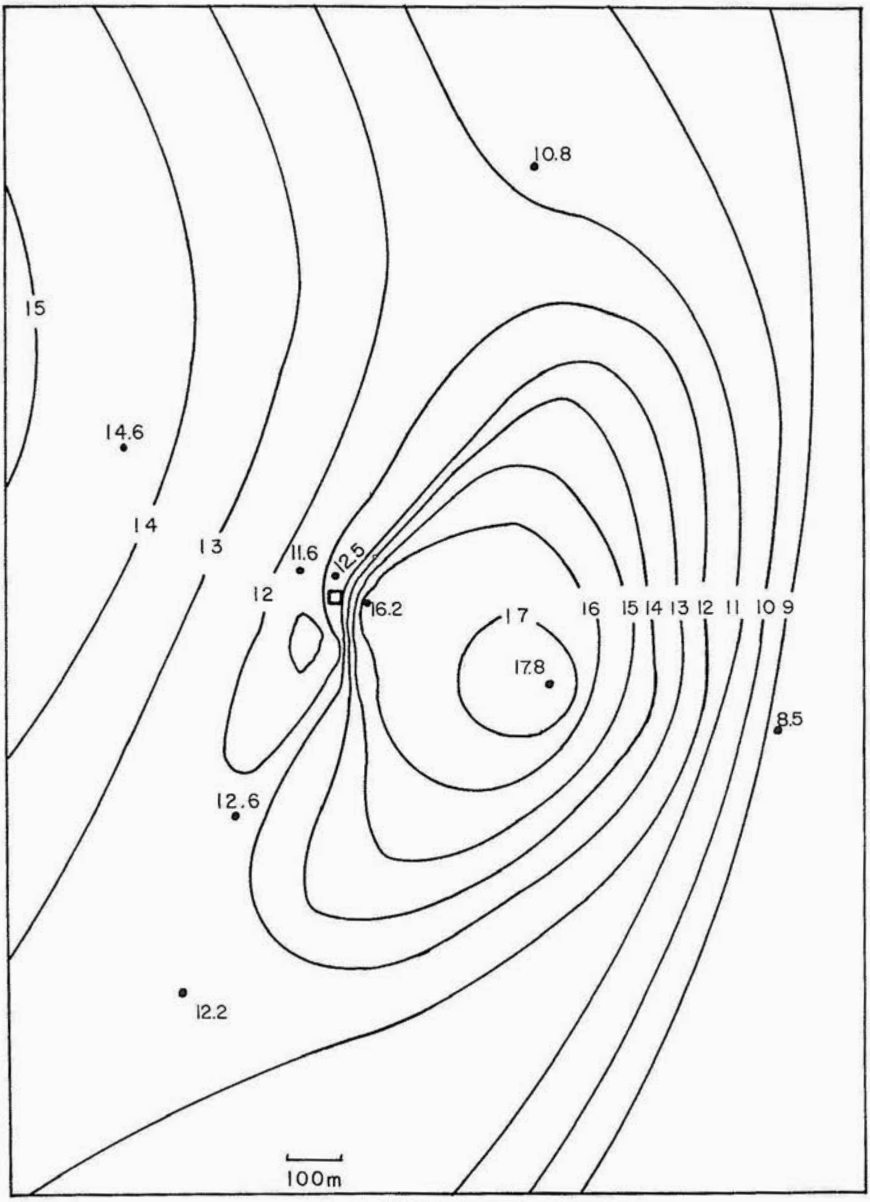

FIG. 2. SEPTEMBER 1972 ORGANIC CARBON ISOPLETHS AROUND PHILO BRICE PLATFORM, an operating platform in Timbalier Bay, Louisiana. Isopleths show that the platform and a source 400 m to the southeast are significant contributors of organic carbon.

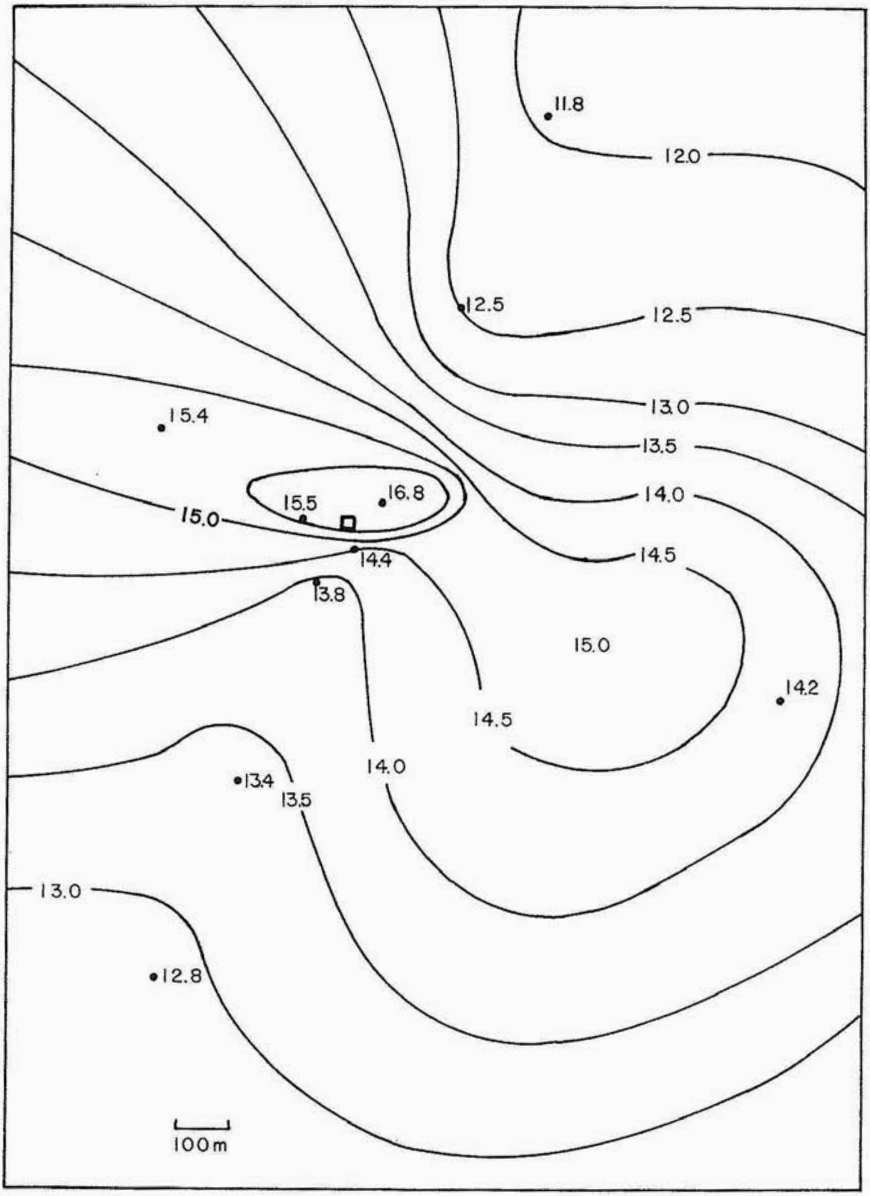

FIG. 3. DECEMBER 1972 ORGANIC CARBON (mg/l) ISOPLETHS AROUND PHILO BRICE PLATFORM indicate that the platform and a source 400 m to the southeast contribute organic carbon to the ecosystem.

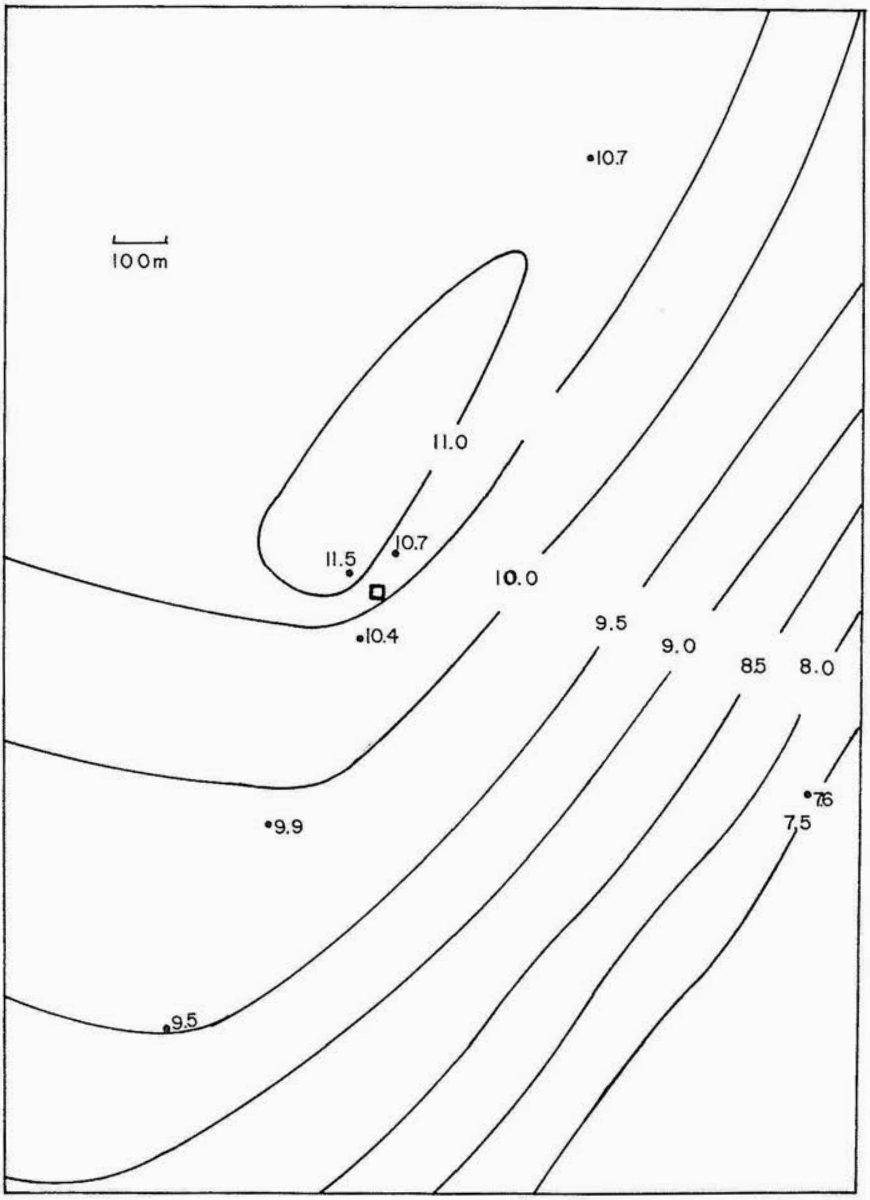

FIG. 4. JANUARY 1974 ORGANIC CARBON (mg/l) ISOPLETHS AROUND PHILO BRICE PLATFORM indicate that the platform is a source of organic material.

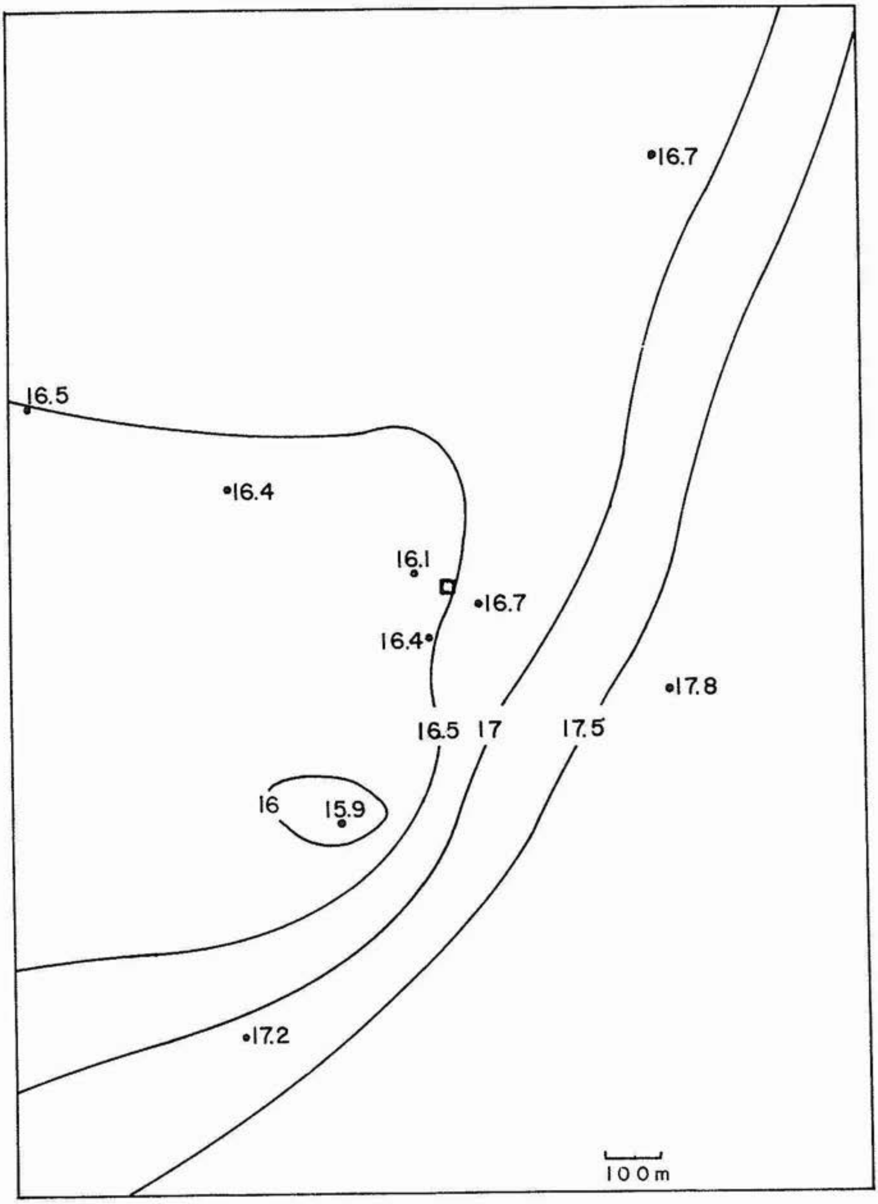

FIG. 5. JANUARY 1973 ORGANIC CARBON (mg/l) ISOPLETHS AROUND PHILO BRICE PLATFORM. Rather uniform high values indicate that the platform is not a major source of organic carbon.

contouring in five intervals of the range of results. The two contour maps were similar. As one proceeds from the east-southeast to the west-northwest along a sampling route, one encounters a rise in OC of 9.3 mg/l in the southeast quadrant to a peak value of 17.8 mg/l, a minimum value of 11.0 mg/l just southwest of the platform and a general increase to 15.5 mg/l in the quadrant northwest of the platform. The effect of oil operations around this platform extends 800 m to the southeast and an indeterminate distance to the northwest, but at least 800 m.

A similar distribution of OC values in this area occurred in December 1972 (figure 3); in this case, however, the maximum increase within the data points was only 5 mg/l to a maximum value of 16.8 mg/l in the vicinity of the platform. Figure 4, indicating the distribution of values obtained in January 1974, more clearly shows the effects of the platform alone. Though the increase noted is only 3.9 mg/l, it is obvious that the platform is the source of this rise in OC levels found primarily in the quadrant northwest of the source.

One set of OC data (figure 5), measured in the Philo Brice Platform area in January 1973, was so uniform that contours did not reveal any significant variations in the OC values. These data represent the highest set of OC values measured in an area this large during the OEI study, 16.6 ± 0.4 mg/l. Wind and wave action was heavy on the bay when these measurements were made.

The OC data collected in Timbalier Bay indicate that an active platform could either increase the surface OC to levels as high as 20 mg/l as in the case of Philo Brice Platform, or decrease the OC far below the mean values measured at the more distant stations, as noted around one of the workover rigs in South Timbalier Bay in January 1974 (figure 6). The latter effect could possibly be explained by dilution processes from well operations or the herding of the surface microlayer neuston away from the platform as an oil slick spreads from its source. The effect often extends 800 m from the rig location. Timbalier Bay production and workover rigs could be described as perturbations in the bay ecosystem causing data collected near structures to have higher standard deviations than data from distant stations showed.

In the offshore domain, the OC data taken alone revealed the presence of platforms on only a few occasions. However, comparing salinity, DO (Oetking et al. 1974), and OC data for a given excursion confirmed that platform effects were being observed. For example, during August 1972, the highest value for OC occurred at the base of Platform 66D (Lat. 28° 49′ 32.8″, Long. 90° 22′ 24.7″). Oetking's dissolved oxygen data also showed that the minimum dissolved oxygen level of 1.0 mg/l occurred near the platform on that date. The general trend of high OC values (greater than 5 mg/l) being associated with low DO measurements

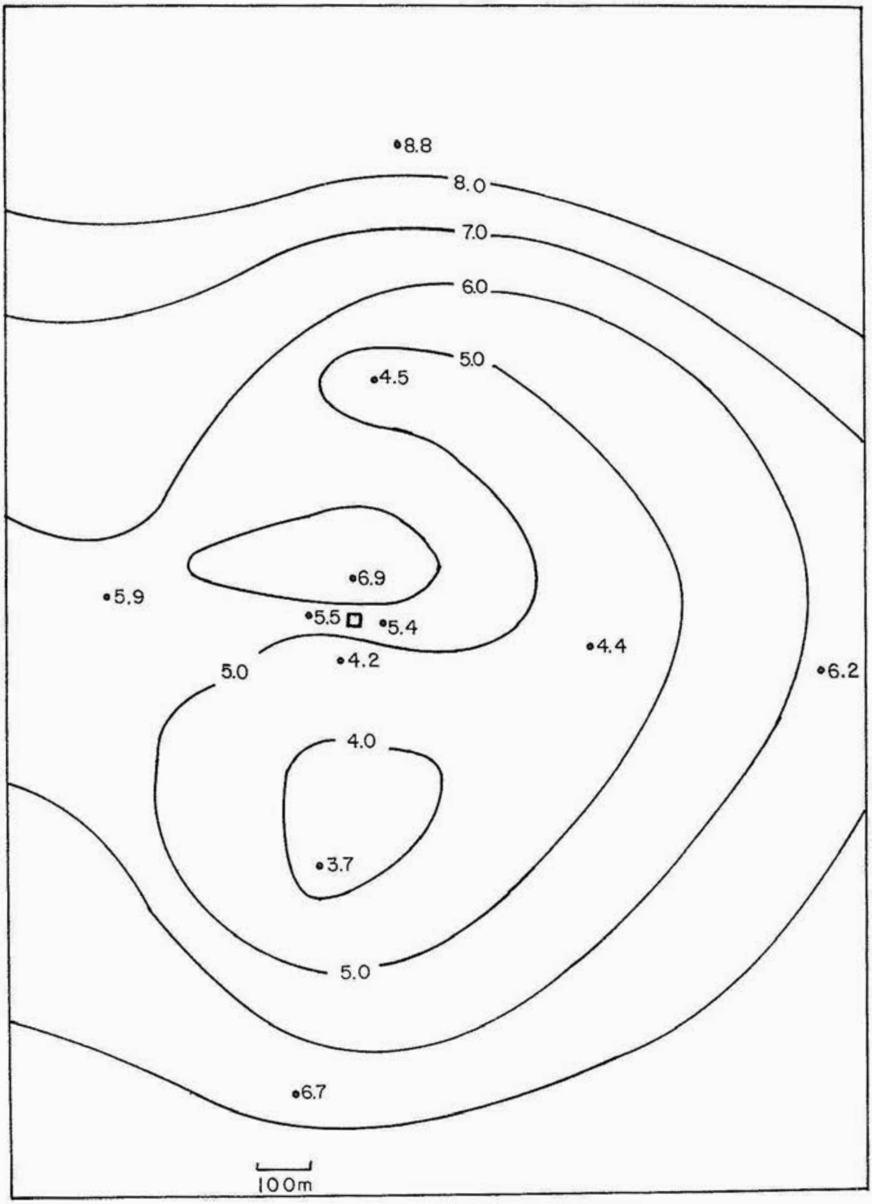

FIG. 6. JANUARY 1974 ORGANIC CARBON (mg/l) ISOPLETHS AROUND A WORKOVER RIG IN SOUTH TIMBALIER BAY. The rig represents a perturbation in the bay ecosystem.

was observed offshore, particularly in the summer months when oxygen depletion rates are high. Data collected around Platform 54A (Lat. 28° 49′ 57.7″, Long. 90° 23′ 24.6″) on July 11, 1974, illustrate this to a degree (figure 7). One of the higher OC (9.8 mg/l) levels occurred at the surface just south of Platform 54A, and some of the lowest DO values occurred beneath that area at a depth of 5 to 7 meters. A high OC value of 9.3 occurred near the bottom at station 30 (Lat. 28° 56.28′, Long. 90° 22.46′) and low dissolved oxygen values accompanied it. A high OC value of 8.8 mg/l occurred near the bottom at station 22 and again low values of DO occurred in this area. Although fewer OC determinations (15 total) were made compared to DO measurements, some of the stratification is indicated by horizontal contours at the 5.0 mg/l OC level at the same depth (5 to 7 m) as an oxygen sagged wedge indicated by Oetking's data.

Platform effects were observable in April 1973 around Platform 26S

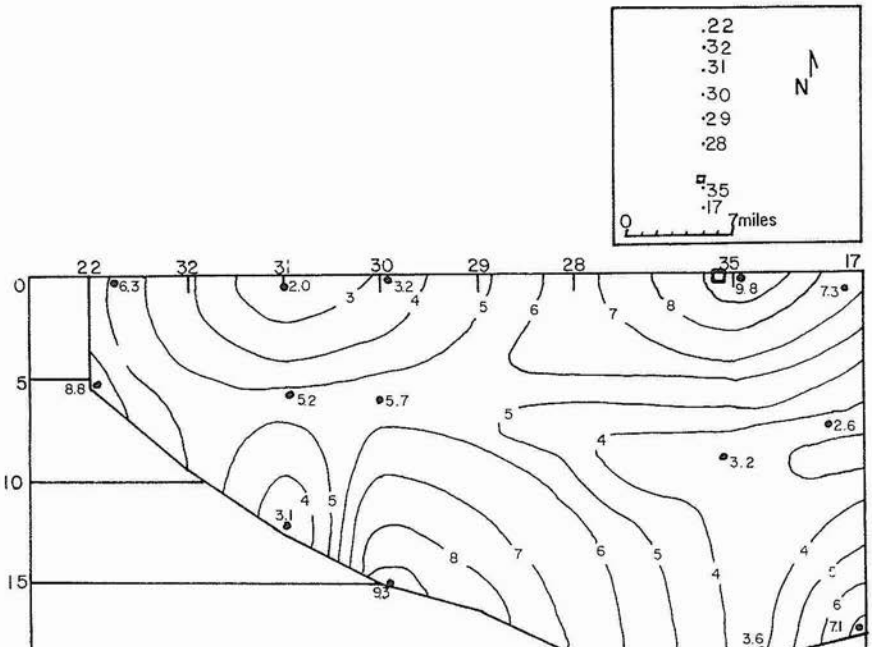

FIG. 7. ORGANIC CARBON VALUES (mg/l) ALONG A LINEAR TRANSECT on the continental shelf passing through Platform 54A sampled on July 11, 1973. Highest surface value measured near platform.

(Lat. 28° 58′ 46″, Long. 90° 10′ 33″) in a synoptic study of two transects that pass through the highly developed oil industry off Grand Isle (figure 8). Comparison of OC contours with salinity, temperature, and DO data (Oetking et al. 1974) revealed general stratification along

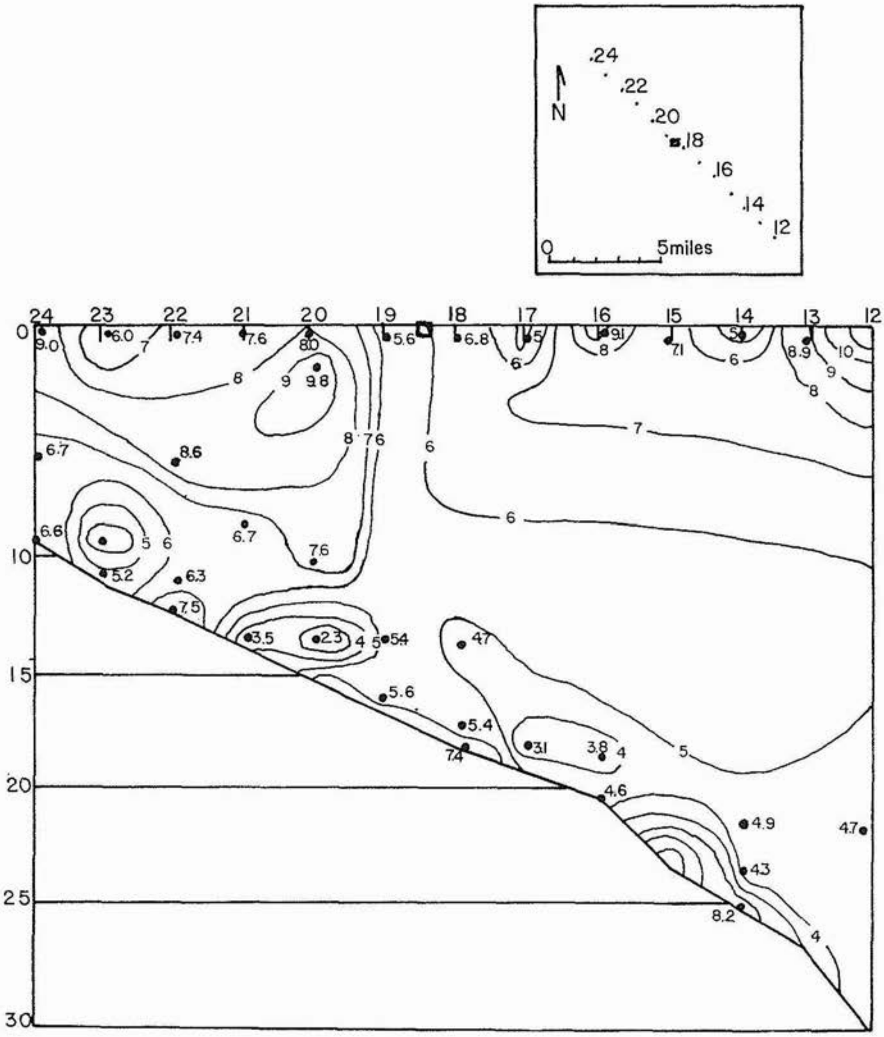

FIG. 8. ORGANIC CARBON VALUES (mg/l) MEASURED ON A TRANSECT BY PLATFORM SH26C, April 6, 1973. Temperature, salinity, and DO values show even more vividly a uniform column of water between stations 18 and 19.

the SE-NW transect except in the vicinity of platform SH26C. There, high salinities extended from the bottom to the surface and all other variables, OC, T, and DO, were nearly uniform from the surface to near bottom. There are at least three plausible reasons for this condition: (1) thermal convection of high salinity waters from the bottom, (2) mixing caused by currents flowing through a platform or platforms, or (3) discharge of brines from well pumping operations. The fact that the high salinity column is so extensive, 2 miles in width, would probably exclude consideration (2) or (3), leaving only thermal convection as a mechanism for the formation of this large vertical column of uniform high salinity water. Whether heat from platforms, heat from a salt dome, or some other mechanism is affecting salinity would require further extensive study. The fact that the phenomenon is associated with a platform suggests that it is caused by the platform.

Except for upper water column measurements where oxygen replenishing occurs, high OC values are accompanied by low DO levels. Platform effects on OC values were usually limited to a maximum distance of 800 to 1600 m.

Unusually high values of OC up to 39.3 mg/l were measured at scattered points within the offshore region during the synoptic study of April 1973. Values as high as 15.4 mg/l were measured for OC in the vicinity of Platform 66D in July and October 1973.

Five-day BOD measurements were made on a large number of selected samples. Oxygen uptake was apparently very slow, resulting in rather low BOD values (0.5 to 5 mg/l). Poor correlation between BOD and OC was observed.

Inorganic carbon values were dependent mostly on pH and salinity in the open Gulf, and upon salinity and stirring in Timbalier Bay.

COD determinations were attempted using mercuric chloride to tie up chlorides and using blanks and standards of equal chlorinity with the set of samples being run. Further, only samples with high OC values were chosen during months when the work load was heavy. COD data did not correlate well with the other variables measured. The poor precision of this measurement obscured real fluctuations in both ecosystems, which were more apparent in the BOD and OC data. This was expected and it confirms the statement in the Environmental Protection Agency's Methods for Chemical Analysis of Water and Waste (1971) that COD's less than 250 are unreliable in saline waters.

SUMMARY AND CONCLUSIONS

OC measurements using a Beckman Model 915 TOC analyzer provide a useful, convenient measure of the total organic load on a marine ecosystem. While DOC and POC determinations (Jeffrey and Hood 1958; Menzel and Vaccaro 1964) may be necessary to detect subtle, low-level changes in OC in the open Gulf, TOC measurements provide a useful assessment of organic enrichment of ecosystems with high organic productivity or loading of a magnitude of 4 mg/l or greater. TOC measurements are very useful when one is dealing with surface samples taken from the top half-centimeter of water surface, where OC values range as high as 20 to 40 mg/l. The TOC analysis in saltwater has become much more convenient and reliable since the incorporation of a factory modification using a ceramic combustion tube in the high temperature channel of the Beckman Model 915 TOC analyzer.

Systematic surface sampling in Timbalier Bay provided data contours whose range from 2 or 3 mg/l to 20 mg/l clearly outlined stationary sources of OC in the vicinity of an operating platform near Philo Brice Island. Other contour maps around workover rigs indicate perturbations in the background OC levels, usually a lowering of OC in the vicinity of the rig. Effects of bay platforms and rigs extended for at least 800 m and beyond.

Offshore investigations revealed OC loading of the marine system from operating platforms and wells ranging from 2 to 4 mg/l above background levels. The effects usually extend some 800 to 1600 m from the platform. The highest value of OC measured in the offshore region was 39 mg/l. Comparing the OEI values with those measured in other marine or aquatic systems (Riley 1937; Duursma 1961; Livingstone 1963; Wilson 1963; Garrett 1967; Williams 1967; Skopints 1968; Brooks et al. 1971; El-Sayed et al. 1972; and Brent et al. 1973) indicates that the offshore area near Grand Isle, Louisiana, is one of the most organic-rich ecosystems in the world of its type, quite atypical for an "open" continental shelf region.

The April 1973 and July 1973 synoptic studies revealed an offshore ecosystem approaching the conditions often found in a freshwater lake or a closed marine system like the Black Sea. Stratification and isolation of deeper waters had occurred along with an algal bloom in April that led to widespread oxygen depletion in waters deeper than 7 m in July. This condition is somewhat surprising since the continental shelf would appear to be an open Gulf ecosystem.

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